Variability of Indicator Values for Ozone Production Sensitivity: A Model Study in Switzerland

A contribution to subproject GLOREAM

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Summary

The threshold values of indicator species and ratios delineating the transition between NO_x and VOC sensitivity of ozone formation are assumed to be universal by various investigators. However, our previous studies suggested that these values may vary according to the locations and conditions. In this study, threshold values derived from various model simulations in Switzerland by the UAM Model are examined using a new approach. Possible definitions for the distinction of NO_x and VOC sensitive O_3 production regimes are given. The dependence of the threshold values of indicators and indicator ratios such as NO_y, O_3/NO_z, $HCHO/NO_y$, and H_2O_2/HNO_3 on the definition of NO_x and VOC sensitivity is discussed. Then, the variation of threshold values under two different meteorological and emission conditions is examined to check how the model responds to changes in environmental conditions. Both perturbed cases – i.e. low emissions and less-stagnant meteorology - lead to similar shifts in threshold values towards more NO_x sensitive chemistry. O_3/NO_z and $HCHO/NO_y$ are predicted to be unsatisfactory as indicators. Although H_2O_2/HNO_3 provides a good separation of NO_x and VOC sensitive regimes, threshold values for this indicator ratio are affected by emission and meteorological perturbations studied in this work.

Introduction

It has been recognised that the dependence of ozone formation on the changes in precursor concentrations is complex and highly non-linear (Seinfeld and Pandis, 1998, Sillman, 1999). The observable species such as NO_y, O_3/NO_z, H_2O_2/HNO_3, and $HCHO/NO_y$ can be used as indicators for ozone sensitivities (Milford et al. 1994, Sillman 1995). The use of indicator species and ratios for assessing the sensitivities of ozone was further explored over different geographical regions by different numerical models (Vogel et al., 1999, Lu and Chang, 1998, Andreani-Aksoyoglu and Keller, 1997). In some cases, threshold values (the transition from NO_x to VOC sensitive regimes) were found to differ from those proposed by Sillman (Lu and Chang, 1998, Andreani-Aksoyoglu and Keller, 1997). These results suggest that threshold values might depend on locations and environmental conditions. Another point to be addressed is the definition of NO_x and VOC sensitive regimes.

Objective

The objective is first to present a new approach to define NO_x and VOC sensitive regimes and then to investigate the changes in threshold values of indicators under perturbed emission and meteorological conditions.

Activities

Model simulations were performed by the Urban Airshed Model (UAM) (Morris and Myers, 1990) using the CBM-IV chemical mechanism (Gery et al., 1989). The simulation period was

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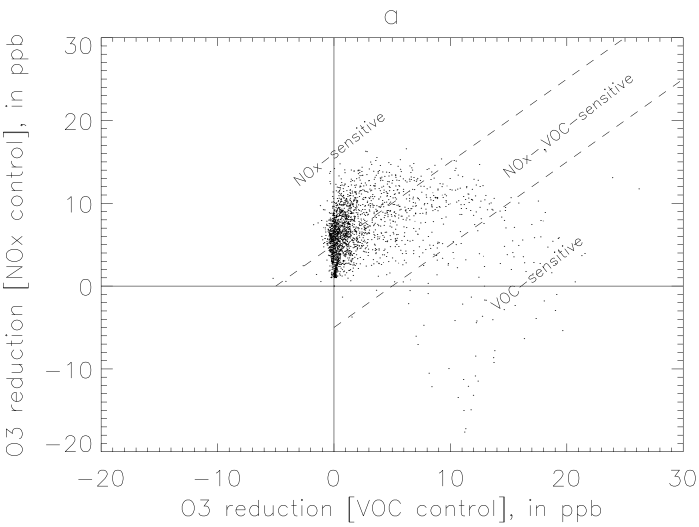
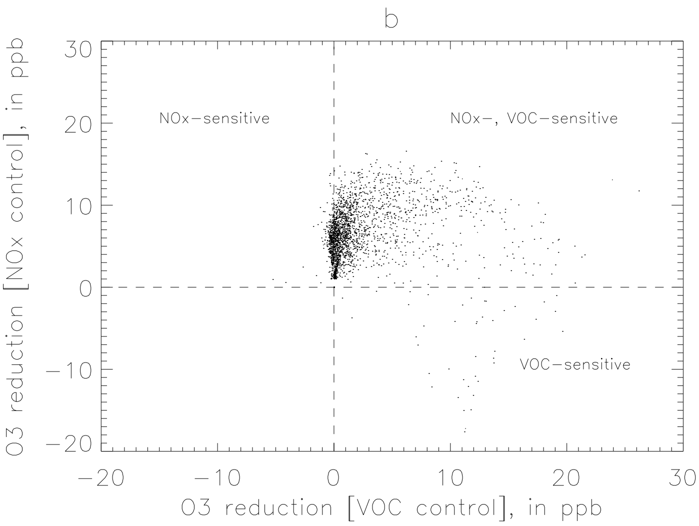
July 27-30, 1993 (Andreani-Aksoyoglu and Keller, 1998). The model domain covered the area of Switzerland with 5 km x 5 km horizontal resolution. The meteorological parameters were obtained from the Swiss Model operated by the Swiss Meteorological Institute and adapted to the model domain. There were 5 vertical layers with varying thicknesses. The model runs, are classified into three groups: base runs (br), runs with low emissions (le) and runs with less-stagnant meteorology (ls).

Results

Sillman (1995) defined NO_x sensitive locations as those where simulated reduction in peak ozone associated with reduced NO_x exceeds the simulated reduction associated with reduced VOC by > 5 ppb. Fig. 1a shows the distribution of various grid cells according to their NO_x, VOC sensitivity using Sillman's definition. This definition shows which control is more effective than the other to reduce peak ozone concentration. Lu and Chang (1998) on the other hand, use another definition which separates extreme cases, i.e. locations where only NO_x or only VOC controls are effective. Their definition is based on zero lines of simulated reduction in peak ozone associated with reduced NO_x, versus reduction associated with reduced VOC (Fig. 1b). According to this definition, most of the grid cells are in the transition range. In this paper, we have modified the approach used by Lu and Chang (1998). Instead of using the zero lines, boundaries with alternating slopes delineating NO_x and VOC sensitivity are examined (Fig.1c).





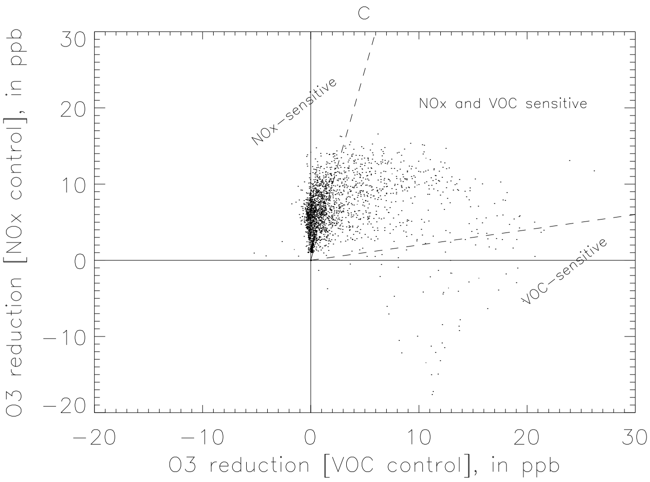


Figure 1. Relation between ozone reductions due to NO_x controls (run 3) and ozone reductions due to VOC controls (run 2) for the base case simulations with UAM in Switzerland.a) using the definition of Sillman (1995), b) using the definition of Lu and Chang (1998), c) using the definition described in this paper

The slopes separating the NO_x sensitive and VOC sensitive regimes from the transition range are defined as ΔO_3[NO_x control]/ΔO_3[VOC control], and ΔO_3[VOC control]/ΔO_3[NO_x control], respectively. As the boundary slope changes, the classification of grid cells may change and the threshold values for distinguishing VOC and NO_x sensitive regimes will vary accordingly. We then investigated how the threshold values depend on the choice of boundary slope (Andreani-Aksoyoglu et al., 2001). The use of boundaries with increasing slope selects fewer grid cells which are NO_x sensitive and the range of NO_x regime varies with changing slope. On the other hand, the range of VOC regime does not change significantly with increasing slope. On the basis of these results a boundary slope of 5 was chosen. Results suggest that NO_x sensitive regime in the model domain can be defined with $NO_y < 6$ (ppb), $O_3/NO_z > 14$, $HCHO/NO_y > 0.29$, $H_2O_2/HNO_3 > 0.7$. Threshold values vary when they are calculated according to the definition of Sillman and Lu and Chang. The threshold values for separating VOC and NO_x sensitive regimes derived from our studies are summarised in Figure 2.

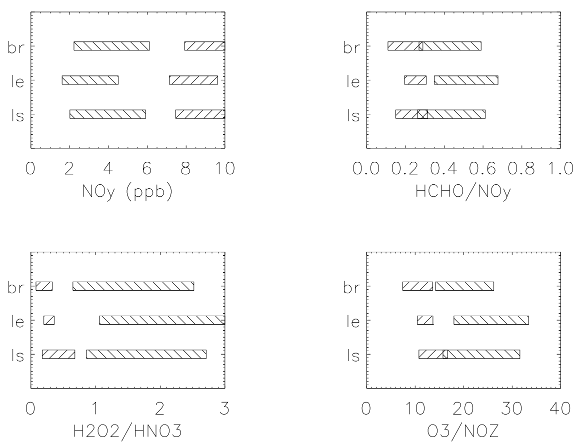


Figure 2. Comparison of threshold values of indicators and indicator ratios for NO_x , VOC sensitivity in various cases : br (base run), le (runs with low emissions), ls (runs with less-stagnant meteorology). Boundary slope=5.

VOC sensitive regime

NOx sensitive regime

In the base case, the NO_x and VOC sensitive regimes are separated except for $HCHO/NO_y$. In the case of low emissions, thresholds of indicator ratios are shifted slightly to higher values, and the threshold of NO_y is shifted to lower values, towards more NO_x sensitive regimes. The gap between the two regimes is wider than in the base case. In the case of less-stagnant meteorology, threshold values of indicator ratios are also shifted slightly to higher values (to lower values for NO_y). Threshold values for the two regimes are overlapped in the case of $HCHO/NO_y$ and O_3/NO_z. In general, NO_y and H_2O_2/HNO_3 seem to be better indicators than the other two. However, it was shown by Sillman (1995) that NO_y does not reflect the uncertainty associated with VOC emission rates and can therefore give misleading results. On the other hand, although H_2O_2/HNO_3 is a successful indicator providing a good separation of NO_x and VOC sensitive regimes, it is affected by the emission and meteorological perturbations.

Conclusions

Threshold values derived from UAM simulations applied to Switzerland are presented using a new approach for separating NO_x and VOC sensitive regimes. The dependence of threshold values for NO_y, $HCHO/NO_y$, H_2O_2/HNO_3, and O_3/NO_z on a wide range of boundary slopes (ratio of ozone reduction due to NO_x control to ozone reduction due to VOC control) is investigated. A boundary slope of 5 is chosen for further analysis of threshold criteria. This slope provides separation of NO_x and VOC sensitive regimes for all indicators. Dependence of threshold values on the definition of NO_x and VOC sensitivity is also shown. Analysis of perturbed simulations can provide useful information on how sensitive the threshold values are and how they change with environmental conditions. Two perturbed cases, low emissions and less-stagnant meteorology, lead to similar shifts in threshold criteria. Specifically, thresholds of NO_y become lower and thresholds of other indicator ratios become higher, showing the tendency towards more NO_x sensitive chemistry. Although H_2O_2/HNO_3 seems to be a successful indicator providing a good separation of NO_x and VOC sensitive regimes, it is affected by the emission and meteorological conditions. $HCHO/NO_y$ and O_3/NO_z seem to be unsatisfactory. Finally, results of this study indicate the necessity to consider the differences in conditions and definitions when applying indicator approach.

Acknowledgements

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